The dry catalytic dehydrogenation of 1-methoxy-2-propanol was also investigated, but no ketone could be isolated. Various attempts to prepare methoxyacetone from chloroacetone using a non-polar solvent also failed.

Two derivatives of methoxyacetone were easily obtained; the 2,4-dinitrophenylhydrazone and the *p*-nitrophenylhydrazone, but the semicarbazone did not form. Attempts to prepare the semicarbazone gave a very insoluble substance, which was proved to be the disemicarbazone of *pyruvaldehyde*. In addition, the osazone of pyruvaldehyde was prepared from phenylhydrazine and methoxyacetone.

Methoxyacetone gave a positive Benedict test (basic medium),[6] a positive Schiff test (acid medium) and a positive test with Tollens reagent (basic medium). Apparently then, methoxyacetone is not too stable in either acid or basic media in the presence of oxidizing agents. This accounts for the rather low yield (28%) in its preparation from Dowanol 33B.

It is probably the rapidity of the reaction of methoxyacetone with 2,4-dinitrophenylhydrazine and *p*-nitrophenylhydrazine, and the insolubility of the resulting derivatives that make their isolation feasible. It is interesting to note that methoxyacetaldehyde also did not give the expected semicarbazone.[7] The product obtained was probably the disemicarbazone of glyoxal.

The authors wish to express their thanks to the Graduate School for providing some funds, to Misses Guy, Hines and Hobbs, for the microanalyses, and to the Dow Chemical Company for a generous sample of Dowanol 33B.

Experimental

Methoxyacetone from 1-Methoxy-2-propanol.—To a solution of 375 g. of sodium dichromate and 202 g. of 1-methoxy-2-propanol (b. p. 118–120° at 745 mm.) in 200 cc. of water was added dropwise over a period of six hours, a solution of 450 g. of sulfuric acid in 115 g. of water. The reaction mixture was stirred during the addition and the temperature kept between 20–25°. After standing at room temperature all night, the green mixture was extracted four times with 200-cc. portions of ether. The ether extract was dried with anhydrous potassium carbonate, the ether removed, and the product fractionated; b. p. 112–116° at 750 mm.; yield 55.5 g. There was also isolated 10 g. of unreacted alcohol. The ketone was carefully refractionated, and the liquid, b. p. 114.5–115.0° at 756 mm., collected; $n^{20}D$ 1.3982, d^{20}_4 0.9494.

The *p*-nitrophenylhydrazone[5] was isolated as yellow-orange plates from alcohol, m. p. 110–111°.

Anal. Calcd. for $C_{10}H_{13}N_3O_3$: N, 18.9. Found: N, 19.2.

The 2,4-dinitrophenylhydrazone was easily formed as yellow-orange needles from alcohol, m. p. 162.5–163°.

Anal. Calcd. for $C_{10}H_{13}N_4O_5$: N, 20.9. Found: N, 20.6.

When 1.0 g. of methoxyacetone, 1.2 g. of semicarbazide hydrochloride and 0.9 g. of sodium acetate were refluxed in 10 cc. of water for three hours, on cooling, 0.6 g. of a white solid was formed. It was insoluble in all common solvents. A sample was recrystallized with great difficulty from a very large volume of water, m. p. 250–254° (dec.). Wohl and Lange[8] noted the insolubility of the disemicarbazone of pyruvaldehyde, and reported a m. p. of 254°, which was not sharp.

Anal. Calcd. for $C_5H_{11}N_3O_2$ (monosemicarbazone of methoxyacetone): N, 29.2. Calcd. for $C_6H_{10}N_6O_2$ (disemicarbazone of pyruvaldehyde): N, 45.1. Found: N, 45.3.

When 1.0 g. of methoxyacetone, 5.0 g. of phenylhydrazine hydrochloride and 7.0 g. of sodium acetate in 40 cc. of water were refluxed for three hours, on cooling, a very viscous dark liquid was formed. This material was easily separated from the water layer by decantation. Crystallization of this liquid from alcohol–water slowly deposited 0.6 g. of an orange solid. Several recrystallizations produced an orange-brown solid, m. p. 147°.[9]

Anal. Calcd. for $C_{10}H_{14}N_2O$ (phenylhydrazone of methoxyacetone): N, 15.7. Calcd. for $C_{15}H_{16}N_4$ (osazone of pyruvaldehyde): N, 22.2. Found: N, 21.7.

Methoxyacetone turned Benedict solution green in ten minutes and a small red precipitate was visible in one-half hour. When a few drops of methoxyacetone were added to 2 cc. of Schiff reagent, a deep purple color was produced immediately. With Tollens reagent, methoxyacetone developed a faint turbidity at room temperature in fifteen minutes, and gave a visible silver mirror in five minutes when heated on a steam-bath.

Attempted Catalytic Dehydrogenation of 1-Methoxy-2-propanol.—1-Methoxy-2-propanol (110 cc.) was passed over brass turnings at a rate of 1.2 cc. per minute. The gas evolution was almost negligible at 400°, increased slightly at 450°, and at 500° the evolution was rapid at first, but then decreased after the first fifteen minutes. At 500°, for instance, 3100 cc. of gas was collected. The product was fractionated and was for the most part unreacted starting material. No 2,4-dinitrophenylhydrazone of methoxyacetone could be isolated from any of the material.

Reactions with Chloroacetone.—Freshly distilled chloroacetone was added to sodium methoxide in benzene and, in another experiment, sodium methoxide was added to chloroacetone in benzene. In both cases, a brown sticky mass was obtained and no methoxyacetone could be isolated.

(6) This result is similar to that obtained with α,α'-diethoxyacetone, which also gave a positive Fehling test; Grimaux and LeFèvre, *Bull. soc. chim.*, [3] **1**, 12 (1889).

(7) Drake, *et al.*, THIS JOURNAL, **60**, 73 (1938).

(8) Wohl and Lange, *Ber.*, **41**, 3615 (1908).

(9) Knopfer reports a m. p. of 148° for the osazone of pyruvaldehyde [*Monatsh.*, **32**, 767 (1911)].

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED MAY 26, 1949

The Sulfonation of *m*-Aminophenol

BY ALFRED L. MILLER,[1] HARRY S. MOSHER,[2] F. W. GRAY AND FRANK C. WHITMORE[3]

The sulfonation of *m*-aminophenol has been reported to yield 2-amino-4-hydroxybenzenesulfonic acid by Oehler.[4] The reference to Oehler's work in Beilstein[5] describes the product as the isomeric 4-amino-2-hydroxybenzenesulfonic acid. Other workers[6,7] who have used the Oehler pro-

(1) Present address: Celanese Corp. of Amer., Summit, N. J.

(2) Present address: Department of Chemistry, Stanford Univ., Calif.

(3) Deceased.

(4) Oehler, German Patent 70,788; *Frdl.*, **3**, 59.

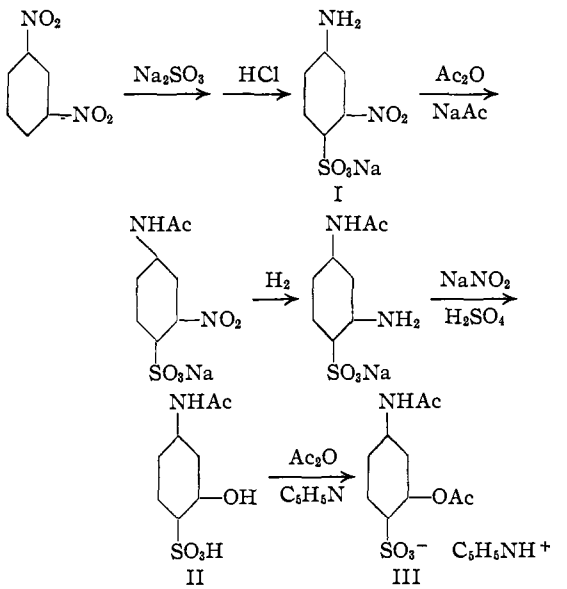
(5) Beilstein, "Handbuch der organischen Chemie," Vol. XIII, 1st ed., Julius Springer, Berlin, 1930, p. 402.

(6) Jacobs, Heidelberger and Rolfe, THIS JOURNAL, **41**, 471 (1919).

(7) Thorpe and Williams, *Biochem. J.*, **35**, 61 (1941).

cedure have reported this latter structure for the product. To the best of our knowledge no structure proof for the product from the sulfonation of *m*-aminophenol has been reported.

In connection with some of our work in the field of synthetic drugs we have determined the structure of this amino-hydroxybenzenesulfonic acid by synthesis through another route as indicated in the series of reactions given. The structure of the intermediate 4-amino-2-nitrobenzenesulfonic acid (I) has been previously established beyond reasonable doubt.[8] Since neither 4-



amino-2-hydroxybenzenesulfonic acid nor the acetyl derivative (II) have definite melting points, comparison was made of the pyridinium-4-acetylamino-2-acetoxybenzenesulfonate (III) derivatives. The products made by the above method and that obtained from the sulfonation of *m*-aminophenol followed by the action of acetic anhydride and pyridine were shown to be identical by a mixed melting point study. This clearly indicates that the structure reported in the Oehler patent is in error and that the stable sulfonation product of *m*-aminophenol is 4-amino-2-hydroxybenzenesulfonic acid as assumed in the other reports.[5,6,7]

Experimental

The Sulfonation of *m*-Aminophenol.—The Oehler procedure[4] consists in heating a solution of one part of *m*-aminophenol in three parts of concentrated sulfuric acid on the water-bath for one hour. The product is obtained by dilution with water. It was converted into the pyridinium acetylaminoacetoxybenzenesulfonate (III) by the method of Thorpe and Williams.[7] After recrystallization from absolute ethanol and ether, it melted at 164–166°.

4-Amino-2-nitrobenzenesulfonic Acid.—A slurry of 86 g. of *m*-dinitrobenzene in 800 ml. of a saturated sodium sulfite solution was prepared and heated until solution was complete. To the hot solution, 250 ml. of concentrated hydrochloric acid was added and the resulting mixture heated at boiling for thirty minutes. The precipitate that formed on cooling was purified by solution and reprecipitation; yellow powder, 50 g.[8,9]

Sodium 4-Acetylamino-2-nitrobenzenesulfonate.—To a slurry of 10.5 g. of 4-amino-2-nitrobenzenesulfonic acid in 30 ml. of glacial acetic acid, sufficient sodium acetate was added to effect solution. After the addition of 30 ml. of acetic anhydride, the acetylation mixture was heated at reflux overnight. One-half of the acetic acid was evaporated and sufficient ether added to cause precipitation. The product was recrystallized from absolute ethanol; 14 g.

Sodium 4-Acetylamino-2-aminobenzenesulfonate.—A solution of 14 g. of sodium 4-acetylamino-2-nitrobenzenesulfonate in 300 ml. of absolute ethanol was shaken with hydrogen in the presence of Adams catalyst at three atmospheres pressure. The reduction was not complete. The precipitate which formed was filtered and purified, 2.5 g. It gave a positive test for an aromatic amine.

4-Acetylamino-2-hydroxybenzenesulfonic Acid.—A solution of 3.5 g. of sodium 4-acetylamino-2-aminobenzenesulfonate in 50 ml. of 3% sulfuric acid was prepared and cooled to 3°. Upon completion of the slow addition of a sodium nitrite solution (1.2 g. of sodium nitrite in 15 ml. of water), 100 ml. of a 1% copper sulfate solution was added and the resulting solution refluxed for one hour. After cooling for several days at 0°, approximately 1 g. of a light brown solid was isolated which gave a negative test for a free amine group and which had no definite melting point.

Pyridinium-4-acetylamino-2-acetoxybenzenesulfonate.—To a pyridine solution of the 1 g. of crude 4-acetylamino-2-hydroxybenzenesulfonic acid was added 1 ml. of acetic anhydride and the resulting precipitate was recrystallized from absolute ethanol and ether, m. p. 164–166°. A mixed melting point with the previously prepared pyridinium salt gave no depression.

We gratefully acknowledge the financial assistance of Parke, Davis and Company in this work.

(8) Nietzke and Helbach, *Ber.*, **29**, 2449 (1896).

(9) Hunter and Sprung, THIS JOURNAL, **53**, 1440 (1931).

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 5, 1949

The Willgerodt Reaction with Acetylphenylacetylene and Benzalacetone

BY DOROTHY NIGHTINGALE AND RICHARD A. CARPENTER[1,2]

The Willgerodt reaction with acetylphenylacetylene and benzalacetone appeared to offer a method for the synthesis of γ-phenylethynylacetic acid and γ-phenylvinylacetic acid. Initial experiments with acetylphenylacetylene and ammonium polysulfide at 190°[3] yielded a product, m. p. 54–56°, containing nitrogen and sulfur which decomposed on standing and was too unstable for consistent analyses. When the reaction was repeated by the procedure of Schwenk and Bloch[4] using morpholine and sulfur, the γ-phenylethynylthioacetomorpholide (I) was obtained in 51% yield. Ozonolysis of (I) followed by oxidative cleavage yielded benzoic acid. All efforts to hydrolyze the thioacetomorpholide to γ-phenylethynylacetic acid were fruitless. Propionylphenylacetylene, morpholine and sulfur yielded an intractable tar.

(1) From the Master's thesis of Richard A. Carpenter.

(2) Present address: Wood River Refinery, Shell Oil Company, Wood River, Illinois.

(3) Wadsworth, Ph.D. Dissertation, University of Missouri (1948).

(4) Schwenk and Bloch, THIS JOURNAL, **64**, 3051 (1942).